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(54) Title: PERFORMANCE ENHANCEMENT IN THE STABILIZATION OF ORGANIC MATERIALS

(57) Abstract: The addition of zinc borate alone or together with a hindered amine light stabilizer and ultra-violet light absorber to organic materials such as thermoplastic polyolefin resin, as is common in wood-plastic composites, provides a substantial reduction in the ultra-violet light degradation of the resin in comparison with similar materials made without zinc borate. This could provide substantial improvements in the long term durability of wood-plastic composites and other organic materials which are used in exterior environments and subject to ultra-violet exposure from the sun.

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**PERFORMANCE ENHANCEMENT IN THE STABILIZATION
OF ORGANIC MATERIALS**

5 This application claims the benefit of provisional application No. 60/585,408, filed July 3, 2004, the entire content of which is incorporated herein by reference.

Field of the Invention

 This invention relates to improvements in the ultraviolet light stabilization of organic materials through the addition of selected borates, and particularly zinc borate.

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Background

 Organic materials exposed to ultraviolet (UV) light undergo degradation, which may change their chemical composition and structure, mechanical properties, surface appearance, and color. This UV aging is associated with natural weathering of plastics, coatings, adhesives, waxes and other special materials exposed to exterior and some interior
15 conditions. Natural and synthetic dyes lose their color and undergo fading when exposed to short wavelength light as well. Natural weathering of materials is a complex process where UV light interaction with matter plays a significant role but may not be the only factor. There are other factors associated with aging of materials containing organic compounds, for example heat or exposure to acidic conditions in the form of acid rain or air contaminants
20 such as sulfur dioxide, etc.

Summary

 In one aspect, the invention provides a method of stabilizing organic material, optionally containing wood particles, against degradation by ultraviolet radiation. This method comprises incorporating from about 0.1 to 5 percent by weight boron compound,
25 preferably zinc borate, boric acid or sodium borate into the organic material possibly containing photoinitiator(s), thereby forming an organic composition with improved light stability. The said percentage of boron compound is based on the total weight of the composition.

In another aspect, the invention provides a method for enhancing the light stabilizing performance of a hindered amine light stabilizer, said method comprising incorporating into an organic material from about 0.05 to 5 percent by weight of a hindered amine light stabilizer and from about 0.1 to 5 percent by weight boric acid salt, preferably zinc borate, and optionally wood particles and/or an ultraviolet light absorber, thereby forming an organic composition with enhanced light stability compared with the same composition without zinc borate, said percentages based on the total weight of the composition.

In yet another aspect, the invention provides a light stabilized composition comprising organic material and from about 0.1 to 5 percent by weight of boric acid salt, preferably zinc borate or sodium borate, and optionally a hindered amine light stabilizer, an ultraviolet light absorber and/or wood particles, said percentage based on the total weight of the composition.

In still another aspect, the invention provides a wood-plastic composite article comprising from about 30 to about 70 percent by weight of a polyolefin selected from the group consisting of polyethylene and polypropylene, from about 30 to about 70 percent by weight wood particles, from about 0.1 to 5 percent by weight boric acid salt, preferably zinc borate, from about 0.05 to 5 percent by weight of a hindered amine light stabilizer, and an ultraviolet light absorber, said percentage based on the total weight of the composition.

Another aspect of the invention provides a method of enhancement of light stabilization performance of abovementioned materials composition, where said materials are exposed to acid environments.

Detailed Description of the Invention

The invention provides a method for reducing ultraviolet (UV) light degradation in organic compositions such as thermoplastic resins through the addition of boron compounds, such as zinc borate, either alone or in combination with a hindered amine light stabilizer (HALS) and optionally a UV light absorber. It has been found, surprisingly, that the addition of zinc borate to many thermoplastic resin compositions, reduced the UV degradation of the resin compositions in comparison with thermoplastic resin made without zinc borate. This improvement in UV light stability was observed with the addition of zinc borate, whether added alone or together with HALS or a HALS/ UV light absorber combination. This could provide substantial improvements in the long-term durability of organic compositions such as

articles made of or containing thermoplastic resin which are used in exterior environments or are subject to substantial UV exposure from many sources, including exposure to sunlight. Examples of such organic compositions which would benefit from this improvement are high density polyethylene resin containing HALS or wood plastic composites containing thermoplastic resin and wood particles.

According to the invention, the addition of between 0.1 and 5% by weight boron compounds, such as zinc borate, and preferably between 1 and 3 %, in the form of a fine powder with a median particle size of 20 microns or less, will provide enhanced protection of organic material against degradation due to UV radiation. A larger quantity of boron compounds, such as zinc borate, will likely give a similar enhancing effect; however, such a high level is generally not preferred due to excessive cost and possible adverse effects on the mechanical properties of polymeric material.

Suitable boron compounds include boric oxide, boric acid, cationic salts of boric acid, or mixtures thereof, and wherein the cations have an atomic or molecular weight less than 130 atomic mass units (AMU). Suitable cationic salts of boric acid include alkali metal borates, such as sodium or potassium borate, alkaline earth metal borates such as calcium or magnesium borate, and transition metal borates, such as zinc borate. Cations with a lower atomic or molecular weight, such as less than 130 AMU, are preferred, as larger cations would tend to reduce the relative proportion of boron, thereby reducing the overall effectiveness of the boron compound. Furthermore, lower solubility boron compounds are preferred, as they reduce the tendency of the borate to leach out when the stabilized compositions are used in wet environments such as exposure to rain in exterior environments. Zinc borate, which has limited solubility in water and a moderate cationic atomic weight, is a preferred boron compound.

Organic materials to which boric acid or boric acid salts such as sodium or preferably zinc borate may be added to improve UV light stabilization include plastics, rubbers, adhesives, coatings, waxes and dyes. Among plastics, polyolefins such as polyethylene and polypropylene are preferred organic materials for use of the methods of the invention, but other resins may also be used. In particular, polyethylene and polypropylene are of special interest with regard to their market importance. They are also used in wood plastic composites. In this application, where a large quantity of wood is present, zinc borate

provides a dual benefit, functioning both as a light stabilizer and as a biocide, protecting wood against decay.

The synergistic improvement resulting from the use of zinc borate for example in combination with HALS in polymeric materials may be observed in a variety of forms. A
5 reduction in oxidation in the polymer chain caused by UV exposure in compositions containing zinc borate in combination with HALS could be very distinct. This difference in oxidation can be detected during testing of polymers with Fourier Transform Infrared Spectroscopy (FTIR). Oxidation of polymers and particularly polyolefins exposed to UV
10 light could be observed in the increase in intensity of infrared absorption bands around 1720 cm^{-1} due to the creation of different quantities of carbonyl groups in the oxidised polymer chain as described in known literature (1. P. Pages, F. Carrasco, J. Saurina, and X. Colom, *Journal of Applied Polymer Science*, Vol.60, p. 153-159 (1996) and 2. S. H. Hamid, A. G. Maddhah, F. S. Qureshi, M. B. Amiu; "Weather Induced Degradation of Polyethylene: Infrared Spectroscopic Studies" *The Arabian Journal of Science and Engineering*, p. 503-531,
15 Volume 13, Number 4, October 1988). The surface of the material may also show increased cracking after exposure to weathering.

In respect to stabilization of polymeric materials containing HALS, preferred hindered amines include bis (2,2,6,6-tetramethyl-4-piperidyl) sebacate, sold under the commercial name Tinuvin[®] 770 (Ciba Geigy), and a mixture of Poly[[6-[(1,1,3,3-
20 tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidiny)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidiny)imino]], butanedioic acid, dimethyl ester, and polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol sold under the commercial name Tinuvin 783 (also from Ciba Geigy). Tinuvin[®]770 is known to be an effective light stabilizer with polymers such as polypropylene, high-density polyethylene,
25 ethylene propylene diene monomer (EPDM) rubber, polystyrene, acrylonitrile butadiene styrene (ABS) terpolymer, styrene acrylonitrile (SAN) copolymer, acrylonitrile styrene acrylate (ASA) and polyurethanes. Similar effects may be achieved by other light stabilizers belonging to the HALS family. Hindered amines are preferably added in concentrations from about 0.1 to 5% by weight of the polymer.

30 Many UV absorbers, for example 2-(2H-Benzotriazole-2-yl)-4 methylphenyl, which is sold under the trade name Tinuvin[®] P (Ciba Giegy) are also useful when added in

combination with the above-described HALS to enhance stabilizer performance. This abovementioned compound is known for its strong light absorbance in the region below 400 nm (e.g. ultraviolet region). Other UV absorbers that are compatible with the polymeric system may also be used.

5 One type of thermoplastic resin-containing article which will benefit from the methods of this invention is woodfiber-plastic composite (also known as wood-plastic composite). Woodfiber-plastic composites typically contain thermoplastic resin binder levels between 30% and 70% by weight of the total composite weight, with the remainder of the substrate comprising about 30-70% by weight wood particles, 1-5% by weight lubricants
10 and other processing additives which are used to help improve the physical properties of the composite product. Woodfiber-plastic composites are generally made by heating the composite mixture so that the thermoplastic resin binder softens, making it pliable or plastic and therefore suitable for shaping, such as by extrusion. Some commonly used thermoplastic resins used in woodfiber-plastic composites include polyethylene, polypropylene and
15 polyvinyl chloride (PVC). High density polyethylene (HDPE) is a preferred thermoplastic resin.

 The woodfiber-plastic composite products are typically manufactured by mixing together all of the components and then heating the mixture above 300°F, e.g. up to about 400°F, in a device capable of additional mixing, such as a twin screw extruder, followed by
20 extrusion through a die, (which may impart fibre orientation and a specific cross-sectional profile to the woodfiber-plastic composite) and then cooling in a water bath. The method of forming woodfiber-plastic composites is well known and is further described in U.S. Patent Nos. 5,516,472 (May 14, 1996), 5,745,958 (May 5, 1998) and 6,153,293 (Nov. 28, 2000), the disclosures of which are incorporated herein by reference.

25 The surface of wood-plastic composites undergoes rapid weathering which is visible under a microscope in the form of crazing and a network of cracks exposing the wood. This is reflected in significant color change, particularly as whitening. Zinc borate has been found to retard the weathering of wood-plastic composites, which is primarily visible as a change in the infrared spectrum of the resin, caused by oxidation. It may be also visible as
30 different color patterns after the exposure of such materials to UV light.

According to the methods of this invention, zinc borate, and optionally HALS and UV absorber, are added to wood-plastic composites in order to reduce photo-oxidation and UV degradation. The zinc borate may be mixed into either the wood particles or the resin prior to manufacture of the wood-plastic composites. HALS and UV absorber, if used, are preferably incorporated in with the resin material.

Tinuvin[®]770 was found to be sensitive to an acidic environment, which significantly reduces its activity. It is likely that many other HALS react similarly. Zinc borate was found to increase the pH of wood-plastic composites. This is likely one of the multiple factors responsible for the decrease in weathering of wood-plastic composites protected by HALS. It is also likely that the acidity of the wood-plastic composites may be increased by acid rain in the natural environment, resulting in even greater benefit from the addition of zinc borate to wood-plastic composites.

Zinc borate may also influence the photo-chemistry of the wood, which is visible through different patterns of color change in wood-plastic composites during weathering. Wood itself is known for a strong sensitivity to weathering and many compounds present in the wood likely act as photo-degradation initiators. Zinc borate may help neutralize these compounds.

Acid is a factor frequently encountered by materials exposed to natural environments. For example, wood is naturally acidic and may contain significant quantities of organic acids. Further increase in the wood acidic nature may be caused by decay fungi. Another example is rain, which has variable acidity depending on the conditions of cloud formation and precipitation. Maps of annual average rain acidity show pH readings in the region of 4.4 across the northeastern US, and significantly lower pH's have been recorded in some parts of Europe. Neutral conditions have a pH of 7.0, and lower pH indicates higher acidity. Many materials exposed to exterior conditions are therefore exposed to acidic conditions, and materials such as wood-plastic composite decking are exposed to acids both from rain and also from the presence of the acidic component in the material. In addition, prolonged exposure to acid rain may lead to the accumulation and concentration of acid in the materials. It is an important consideration that many UV stabilizers, such as several HALS compounds, are reactive with acid and seem to show decreased activity in acidic conditions. The inherently acidic conditions of exterior exposure are also frequently not taken into

consideration when materials are tested for weathering resistance in laboratory or even many exterior exposure experiments

It is also expected that enhancement of light stabilization of organic materials by the combination of zinc borate with HALS packages containing hindered amines, UV absorbers, applies not only to polymeric materials, but also dyes and pigments. Polymeric materials which are stabilized with a combination of zinc borate and HALS may be used in a mixture with a variety of other components, for example, pigments, mineral or organic fillers, fire retardants, lubricants, blowing agents and other types of compatible stabilizers. In the case of the organic filler used in a plastic matrix, for example wood in wood plastic composite, zinc borate will supply additional protection against decay fungi. It is also expected that zinc borate may stabilize some materials by interaction with certain potential UV degradation initiators, removing them from the environment this way. On the other hand, it was also found that zinc borate does not seem to absorb UV radiation efficiently. The protection of materials against weathering in this manner, as is known for many pigments for example titanium dioxide or zinc oxide, is not a likely factor here.

The invention can be further explained in the following examples:

EXAMPLES

Example 1

Wood-plastic composite board samples were prepared by blending and extruding the thermoplastic material compositions listed in Table 1. The extruder used was a twin screw with 5 heating zones and a sheeting profile die designed for the extrusion of wood-plastic composites. The extrusion temperature was 345°F. The extruded boards, measuring 150 mm in width and 12 -25 mm in thickness, were cooled on-line by sprayed water.

Table 1. Components of wood-plastic composite board samples tested (percent by weight)

Sample #	Wood Flour		HDPE Resin ⁽³⁾	UV Stabilizer Package ⁽⁴⁾	Zinc Borate ⁽⁵⁾	Lubricants ⁽⁶⁾	Talc ⁽⁷⁾
	Pine ⁽¹⁾	Oak ⁽²⁾					
1	49.79	-	36.97	9.24 ^(a)	0	3.0	1.0
4	47.54	-	36.37	9.09 ^(a)	3.0	3.0	1.0
5	51	-	45	0	0	3.0	1.0
6	48.71	-	44.29	0	3.0	3.0	1.0
8	65.93	-	24.06	6.01 ^(a)	0	3.0	1.0
11	63.42	-	23.66	5.92 ^(a)	3.0	3.0	1.0
27	-	48.28	36.58	9.14 ^(a)	2.0	3.0	1.0
28	-	49.79	36.97	9.24 ^(a)	0	3.0	1.0
29	-	48.28	36.58	9.14 ^(b)	2.0	3.0	1.0
31	-	64.26	27.39	5.95 ^(a)	2.0	3.0	1.0
33	-	65.93	24.06	6.01 ^(a)	0	3.0	1.0

(1) Wood flour grade 2020 (American Wood Fibers Inc.)

(2) Wood flour grade 3720 (American Wood Fibers Inc.)

5 (3) HDPE – resin B-53 35H flakes (Solvay)

(4) UV stabilizer packages:

(a) Tinuvin[®] 770 (Ciba Geigy) 5 wt.%, Tinuvin[®] P (Ciba Geigy) 5 wt.%, metal oxides pigments–15 wt.%, HDPE (carrier) – 75 wt.%

10 (b) Tinuvin[®] 783 (Ciba Geigy) 5 wt.%, Tinuvin[®] P (Ciba Geigy) 5 wt.%, Metal oxides pigments–15 wt.%, HDPE (carrier) – 75 wt.%

(5) Zinc borate – Borogard[®] ZB (U.S. Borax Inc.)

(6) Lubricants - blend of:

- zinc stearate (Ferro Chemical) – 67 wt.%
- EBS Wax (GE Specialty Chemicals) – 33 wt.%

15 (7) Talc – Nicron 403 (Luzenac America Inc.)

Example 2

20 Wood plastic composite mouldings were prepared by blending and extruding the thermoplastic material composition containing polypropylene resin, pine wood, lubricants, talc and optionally HALS, UV absorber and zinc borate as listed in table 2. The extruder used was a twin screw with five heating zones and a moulding profile die designated for extrusion of wood plastic composites. The extrusion temperature was about 380°C. The extruded mouldings measuring 37 mm in width and 9 mm in thickness were cooled on line by sprayed

25 water.

Table 2. Components of wood plastic composite molding samples tested

Sample #	Wood Flour Pine	PP Resin	UV Stabilizer Package ⁴	Zinc Borate	Lubricants	Talc
301	50	46	-	0	3	1
302	48	46	-	2	3	1
309	50	41	5 ^c	0	3	1
310	48	41	5 ^c	2	3	1
311	50	43.5	2.5 ^c	0	3	1
312	48	43.5	2.5 ^c	2	3	1
315	50	36	10 ^d	0	3	1
316	48	36	10 ^d	2	3	1

⁴ UV stabilizer packages:^c Tinuvin[®] 770 (Ciba Giegy) 5% wt, Tinuvin P (Ciba Giegy), 5 PBW, PP (carrier) 90% wt^d Tinuvin[®] 783 (Ciba Giegy) 5% wt, PP (carrier) 95% wt**Example 3**

High density polyethylene Escorene HD6706 (Exxon) was blended with Tinuvin[®] 770, or Tinuvin 783[®]. To selected blends, zinc borate, anhydrous borax or boric oxide was added as listed in table 3. All additives were prepared earlier in the form of masterbatches. Dry blends were extruded using Brabender ¾" single screw extruder equipped in mixing screw and strand die. The extruded strand was pelletized using a strand pelletizer. Plastic sheets with thickness 0.5 mm were moulded from plastic pellets using a hot press at 180°C. Moulded sheets were cooled with cold water while still under pressure.

Table 3. Components of polyethylene sheeting

Sample #	HDPE	UV Stabilizer Package ¹	Borate Masterbatch ²	Borate Compound
041104-1	100	-	-	-
041104-4	84	-	16 ^j	zinc borate
041104-5	94	6 ^e	-	-
041105-3	78	6 ^e	16 ^j	zinc borate
050505-1	94	6 ^e	-	-
050505-8	78	6 ^e	16 ^j	ZB
050505-9	78	6 ^f	16 ^h	boric oxide
050505-11	78	6 ^e	16 ^j	zinc borate
050505-12	84	-	16 ^h	boric oxide
050505-13	84	-	16 ⁱ	sodium borate

¹UV stabilizer package:e – Tinuvin[®] 770 (Ciba Geigy) 5% wt, HDPE 95% wtf – Tinuvin[®] 783 (Ciba Geigy) 5% wt, HDPE 95% wt

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²Borate masterbatch:

h. Boric oxide (US Borax) 25% wt, HDPE 75% wt

i. Anhydrous sodium borate (US Borax) 25% wt, HDPE 75% wt

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j. Borogard ZB[®] zinc borate (US Borax) 25% wt, HDPE 75% wt**Example 4**

For accelerated weathering specimens measuring 70 mm x 100 mm were cut from the extruded boards made in Example 1. Moldings made in example 2 were cut to 100 mm in length and multiple specimens assembled in weatherometer window frames. Plastic sheets made in example 3 were cut into strips 25 mm width and 100 mm in length and also assembled in weatherometer frames. The specimens were then exposed in a QUV chamber according to ASTM G-154 Specimens were periodically monitored to record progress in weathering and any sudden changes in their appearance. Exposure conditions were as follows:

- (A) 8 hours UV light (UVA 340 lamps with irradiance 0.68 w/m²/nm) at 60°C, 5 minutes water spray, 3 hours 55 min. condensation at 50°C.
- (B) 8 hours UV light UV light (UVA 340 lamps with irradiance 0.77 W/m²/nm) at 60C , 4 hours condensation cycle and 2 hours soak in distilled water or

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sulfuric acid solution with pH 3 followed by 2 hours drying at 23°C every 24 hours. instead of condensation.

- (C) 8 h UV light (UVB 313 EL lamps with irradiance 0.77 W/m²/nm) at 60°C and 4 hours condensation cycle at 50°C.
- 5 (D) 8 hours UV light (UVB 313 lamps with irradiance 0.77 W/m²/nm) at 70°C and 4 hours condensation cycles at 50°C.

Example 5

Samples of wood plastic composites were exposed to sun in exterior conditions in
10 Vancouver, British Columbia (condition Vr in table 4) and Valencia, California (condition Va in table 4) for a period of one year. In addition to natural moisture, samples exposed in Valencia were additionally sprinkled with approximately 0.5 inch of water per day in the form of lawn irrigation.

Example 6

15 Specimens having 0.5 mm thickness were cut from the board samples prepared in Example 1 and exposed to 2000h accelerated weathering as described in Example 4. These 0.5 mm thick specimens with one surface exposed to weathering were then broken into small pieces and approximately 0.3 g of material was placed in a 200 mesh stainless steel pouch. The pouch was placed in a round-bottomed flask with 100 ml of xylene [xylene isomers plus
20 ethyl benzene b.p. 136 – 140°C (Sigma-Aldrich)] with 1% suitable antioxidant and boiled under condenser for 8h. After completion of heating, hot liquid was transferred to a beaker and 15 mL of heptane [Heptane 95%, b.p. 98°F (Sigma Aldrich)] was added dropwise with mixing. Mixture was cooled and precipitated polymer was filtered, washed and dried. Thin film specimens, 50 µm in thickness, were compression moulded from dry resin at 175°C.

25 FTIR transmission spectra were acquired for resin obtained from reference sample (non-exposed) and three exposed samples as mentioned above. IR absorption bands intensity measurements on infrared spectra, evaluated as described in Example 7 are shown in Table 4 and 5.

Table 4. Photo-oxidation of polymeric material samples, with and without borate compounds, exposed to weathering at different conditions

Exp't #	Sample pairs	Composition			Weathering			FTIR		T-test (95%)	Comments
		Resin type	HALS	Wood	Conditions	Period	Environment	Without ZB	With ZB		
I	1 & 4	HDPE	+	+	A	300h	acid	0.241	0.120	different	ATR
II	1 & 4	HDPE	+	+	A	500h	acid	0.251	0.165	different	ATR
III	1 & 4	HDPE	+	+	A	500h	distilled water	0.229	0.140	different	ATR
IV	1 & 4	HDPE	+	+	B	2000h	NA	0.288	0.318	NA	ATR
V	1 & 4	HDPE	+	+	B	2000h	NA	1.338	2.167	NA	TRANS
VI	1 & 4	HDPE	+	+	ext (Va)	1 year	NA	0.137	0.120	different	ATR
VII	1 & 4	HDPE	+	+	ext (Vr)	1 year	NA	0.228	0.186	different	ATR
VIII	1 & 2	HDPE	+	+	ext (Va)	1 year	NA	0.137	0.122	different	ATR
IX	2 & 4	HDPE	+	+	ext (Va)	1 year	NA	0.122	0.120	different	ATR
X	5 & 6	HDPE	-	+	A	300h	acid	0.375	0.296	different	ATR
XI	5 & 6	HDPE	-	+	A	500h	acid	0.397	0.326	different	ATR
XII	5 & 6	HDPE	-	+	A	500h	distilled water	0.398	0.317	different	ATR
XIII	5 & 6	HDPE	-	+	ext (Va)	1 year	NA	0.163	0.159	ambiguous	ATR
XIV	5 & 6	HDPE	+	+	B	2000h	NA	NA	0.378	NA	ATR
XV	5 & 6	HDPE	+	+	B	2000h	NA	5.943	3.961	ambiguous	TRANS
XVI	8 & 11	HDPE	-	+	B	2000h	NA	2.562	1.333	NA	TRANS
XVII	27 & 28	HDPE	+	+	A	500h	acid	0.163	0.127	different	ATR
XVIII	27 & 28	HDPE	+	+	A	500h	distilled water	0.156	0.104	different	ATR
XIX	27 & 28	HDPE	+	+	B	100h	NA	0.086	0.084	NA	ATR
XX	27 & 28	HDPE	+	+	B	2000h	NA	2.600	2.230	NA	TRANS
XXI	29	HDPE	+	+	B	2000h	NA	0.087	NA	NA	ATR
XXII	31 & 33	HDPE	+	+	B	2000h	NA	2.419	1.059	ambiguous	TRANS

Table 4. (continued)

Exp't #	Sample pairs	Composition			Weathering			FTIR		T-test (95%)	Comments
		Resin type	HALS	Wood	Conditions	Period	Environment	Without ZB	With ZB		
XXIII	301&302	PP	-	+	A	356h	acid	0.813	0.851	ambiguous	ATR
XXIV	301&302	PP	-	+	A	356h	distilled water	0.910	0.775	different	ATR
XXV	311&312	PP	+	+	A	356h	acid	0.859	0.685	different	ATR
XXVI	311&312	PP	+	+	A	500h	distilled water	0.846	0.818	ambiguous	ATR
XXVII	315&316	PP	+	+	A	500h	acid	0.640	0.714	different	ATR
XXVIII	315&316	PP	+	+	A	500h	distilled water	0.658	0.662	similar	ATR
XXIX	041104-1 & 041104-4	PE	-	-	D	155h	NA	3.308	2.807	different	TRANS.
XXX	050505-8 & 050505-9*	PE	-	-	D	155	NA	1.689	0.104*	different	TRANS
XXXI	041104-1 & 050505-12*	PE	-	-	D	155h	NA	3.308	2.372*	different	TRANS
XXXII	041104-1 & 050505-13**	PE	-	-	D	155	NA	3.308	0.589**	different	TRANS
XXXIII	041104-5 & 041105-3	PE	-	-	C	1000h	NA	0254	0.109	different	TRANS
XXXIV	041104-5 & 041105-3	PE	-	-	C	1500h	NA	0.683	0.330	different	TRANS
XXXV	050505-1 & 050505-11	PE	-	-	D	700h	NA	1.333	0.886	similar	TRANS

*Boric Acid

**Sodium Borate

subsequently referred to as the Height Indicator of Photooxidation. T-tests were applied to data obtained for pairs of equivalent samples with and without borates (or, for certain tests, HALS) to distinguish results. Sample pairs were judged different from each other if the t-test met or exceeded a 95% confidence interval.

- 5 In the infrared transmittance spectral analysis, the height of the band at around 1720 cm^{-1} was measured as an indicator of the creation of carbonyl groups in the polymer, as is known to be a result of photo-degradation. To correct any small variation in sample thickness, the selected reference peak height was measured as well, and the ratio of the peaks was calculated. (Height Indicator of Photooxidation)
- 10 Decreased oxidation of the HDPE (high density polyethylene) or PP (polypropylene) plastic is visible as a decrease the height of the absorption band at around 1720 cm^{-1} . In some cases, the result of this improvement in stabilization was seen as decreased color change or reduced surface degradation in the form of cracking, as is visible in sample #27. Results comparing the performances of tested samples in respect to relative height of absorption band
- 15 at around 1720 cm^{-1} for pairs of similar samples with and without zinc borate (or, for certain tests, HALS) made according to examples 1, 2 and 3 and exposed to weathering according to Example 4 and 5 are shown in Table 4.

Lower IR absorption bands in the carbonyl group region for transmittance or absorbance spectra indicates reduced oxidation of the HDPE plastic resin. The addition of zinc borate to plastic compositions with and without hindered amine light stabilizer (HALS), reduced polyethylene oxidation caused by UV radiation. These results show a substantial reduction in photo-oxidation of polyethylene in wood-plastic composites when 2-3% by weight zinc borate is added.

Example 7

Exposed specimens were assessed for their degree of polymer photooxidation based on FTIR data and optionally for color change and degree of surface degradation. Evaluations were conducted as follow:

1. Color change (ΔE) according to ASTM D2244 using Gretag-Macbeth spectrophotometer (Measurement conditions: color equation LCH, angle 10 deg., Illuminant D 65, reflectance mode with regular aperture).
2. Degree of surface degradation based on microscopic evaluation (under magnification 25-100x) using a Leica MZ-12 stereoscopic microscope
3. Photo-oxidation was assessed based on the infrared absorbance band in the 1720 cm^{-1} region. IR spectra were obtained using an AVATAR FTIR Spectrometer (Thermo-Nicolet). For the ATR method applied to wood plastic composite surface, the Split Pea[®] accessory was used. Peak height corrections were conducted using the 1470 cm^{-1} region absorption band as the reference for polyethylene and 1160 cm^{-1} for polypropylene. An additional correction factor was also introduced to the reference peak in polyethylene spectra in respect to crystallinity. 27 ATR spectra were collected for each sample and averaged prior to evaluation. For the transmission method applied to 0.5 mm thick plastic strips, absorbance spectra were again evaluated at around 1720 cm^{-1} , with the 2018 cm^{-1} region absorption band as the reference. Three strips were evaluated for each composition, with five spectra acquired for each strip. All fifteen spectra were averaged prior to analysis. For all methods, results are presented as a ratio of the 1720 cm^{-1} absorption peak height to the selected reference peak height. This is

Table 5. Evaluation of properties of wood plastic composites containing HALS, with and without zinc borate, after exposure to accelerated weathering

Sample #	Zinc borate content %	Accelerated Weathering Exposure					
		100 hours			2000 hours		
		Color Change ΔE	Degree of surface degradation*	Height indicator of photo-oxidation	Color Change ΔE	Degree of surface degradation*	Height indicator of photo-oxidation
1	0	1.0	1-2		5.1	7-8	0.318
4	3	1.2	1-2		5.4	7-8	0.288
5	0	2.4	-	0.231	26.7	-	0.378
6	3	1.5	-		26.7	-	
8	0	2.5	-		5	-	
11	3	4.8	-		4.6	-	
27	2	0.8	1	0.086	7.6	5	0.260
28	0	2.2	1-2	0.084	12.6	7-8	0.312
29	2	0.3	1	0.087	8.9	5-6	-
31	2	3.3	-		15.5	-	-
33	0	4.8	-	-	15.5	-	-

*Assessment of surface degradation based on scale from 0 to 10
(0 - no change to the surface, 10 - very strong degradation).

5 ** Increased absorbance is directly related to increased polymer oxidation by the UV induced degradation process.

Results:

10 An evaluation of infrared (IR) absorbance spectra was made for all samples, and the results compared for pairs of samples as described in Table 4. The addition of borates to polymeric materials made without wood improves the UV resistance of those materials, as is seen in Experiments XXIX, XXXI, and XXXII in Table 4. Some borates, in particular ZB, also show synergistic effects with HALS in increasing the UV resistance of polymeric materials, as is shown in Experiments XXXIII, XXXIV, and XXXV in Table 4. Wood-
15 plastic composite materials made without HALS also show increased UV resistance with the addition of ZB, as is shown in Experiments X through XVI, XXII, XXIII, and XXIV in Table 4. Wood-plastic composite materials containing both ZB and HALS show a synergistically increased resistance to UV radiation, as is seen in Experiments I-IX, XVII-XX, XXII, , and XXV in Table 4. The increased UV resistance of WPC materials in the presence of ZB, both
20 with and without HALS, is also observed in acidic conditions, as is shown in Experiments I,

II, X, XI, XVII, XXIII, and XXV in Table 4. Such evaluation statistically confirm data shown in table 5

5 The color change was evaluated for all polyethylene WPC samples subject to accelerated weathering at 100 hours and 2,000 hours accelerated weathering, with somewhat mixed results. Samples #5&6 (pine without HALS) and samples #31&33 and #27, 28 &29 (oak with HALS) showed less color change at 100h with zinc borate than without, while sample pairs #1&4 and #8&11 (both pine with HALS) indicated more color change with zinc borate. At 2,000 hours samples #27, 28 &29 again showed substantially greater resistance to color change with zinc borate than without, while sample pair #1&4 indicated slightly more color change with zinc borate. Color change in WPC materials, however, may be due to the photo-oxidation of chromophores present in the wood as well as to photo-oxidation of the polymer binder.

15 Surface degradation was evaluated on only two sample pairs. Samples #27, 28 &29 (about 50% oak with HALS) showed less surface degradation with zinc borate than without, especially after 2,000 hours accelerated weathering, while sample pair #1&4 (about 50% pine with HALS) seems to show no difference with and without zinc borate. Both pairs of samples show significantly less photodegradation with ZB when tested by FTIR spectroscopy.

20 Height Indicators of Photooxidation were measured on sample pairs #5&6 (about 50% pine without HALS), #1&4 (about 50% pine with HALS), and #27&28 (about 50% oak with HALS), after 2,000 hours weathering. (table 4 and 5). In each case the IR results indicated less photo-oxidation with zinc borate than without. Sample pair # 27&28 also showed better results with zinc borate after 100 hours weathering. In fact, sample pair #27&28 yielded better results with zinc borate at both accelerated weathering times by all three evaluation methods (color change, surface degradation and IR determination of photo-oxidation).

25 Various changes and modifications of the invention can be made and to the extent that such changes and modifications incorporate the spirit of this invention, they are intended to be included within the scope of the appended claims.

CLAIMS

5 What is claimed is:

1. A method of stabilizing organic material against degradation by ultraviolet radiation, said method comprising incorporating from about 0.1 to about 5 percent by weight boron compound into the organic material, thereby forming a light stabilized organic
10 composition, said percentage based on the total weight of the composition, wherein the boron compound comprises boric oxide, boric acid, cationic salts of boric acid, or mixtures thereof, and wherein the cations have an atomic or molecular weight less than 130 atomic mass units (AMU).
2. The method according to claim 1 wherein the boron compound is zinc borate.
- 15 3. A method of stabilizing organic material exposed to acidic environmental conditions in a pH range of about 2 to about 5 against degradation by ultraviolet radiation, said method comprising incorporating from about 0.1 to about 5 percent by weight boron compound into the organic material, thereby forming a light stabilized organic composition, said percentage based on the total weight of the composition, wherein the boron compound
20 comprises boric oxide, boric acid, cationic salts of boric acid, or mixtures thereof, and wherein the cations have an atomic or molecular weight less than 130 atomic mass units (AMU).
4. The method according to claim 3 wherein the organic material is selected from the group consisting of plastics, rubbers, adhesives, coatings, waxes and dyes.
- 25 5. The method according to claim 3 wherein the boron compound is zinc borate.
6. The method according to claim 5 wherein the organic material is a polyolefin selected from the group consisting of polyethylene and polypropylene.
7. The method according to claim 6 wherein the polyolefin and zinc borate are mixed with wood fibers, thereby forming a wood-plastic composite, said composite having
30 improved stability against degradation by ultraviolet radiation.

8. The method according to claim 7 wherein the wood-plastic composite contains from about 1 to about 3 percent by weight zinc borate, said percentage based on the total weight of the composite.

9. A method for enhancing the light stabilizing performance of a hindered amine light stabilizer, said method comprising incorporating into an organic material from about 0.05 to 5 percent by weight of a hindered amine light stabilizer and from about 0.1 to 5 percent by weight zinc borate, thereby forming an organic composition with enhanced light stability compared with the same composition without zinc borate, said percentages based on the total weight of the composition.

10. A method for enhancing the light stabilizing performance of a hindered amine light stabilizer under exposure to acidic environmental conditions in a pH range of about 2 to about 5, said method comprising incorporating into an organic material from about 0.05 to 5 percent by weight of a hindered amine light stabilizer and from about 0.1 to 5 percent by weight zinc borate, thereby forming an organic composition with enhanced light stability compared with the same composition without zinc borate, said percentages based on the total weight of the composition.

11. The method according to claim 10 wherein the organic material is selected from the group consisting of plastics, rubbers, adhesives, coatings, waxes and dyes.

12. The method according to claim 10 wherein the composition contains from about 0.1 to 2 percent by weight of a hindered amine light stabilizer and from about 1 to 3 percent by weight zinc borate, said percentages based on the total weight of the composition.

13. The method according to claim 10 wherein the hindered amine light stabilizer is bis (2,2,6,6-tetramethyl-4-piperidyl) sebacate or a mixture of poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidiny)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidiny)imino]], butanedioic acid, dimethylester, and polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol.

14. The method according to claim 13 wherein the organic material is a polymer selected from the group consisting of polypropylene, polyethylenes, ethylene propylene diene monomer (EPDM) rubber, polystyrene, acrylonitrile butadiene styrene (ABS) terpolymer, styrene acrylonitrile (SAN) copolymer, acrylonitrile styrene acrylate (ASA) and polyurethanes.

15. The method according to claim 10 wherein the organic material is a polyolefin selected from the group consisting of polyethylene and polypropylene.

16. The method according to claim 15 wherein the polyolefin, zinc borate and hindered amine light stabilizer are mixed with wood fibers, thereby forming a wood-plastic composite with enhanced light stability compared with the same composite without zinc borate.

17. The method according to claim 10 wherein an ultraviolet light absorber is also incorporated into the organic material.

18. A light stabilized composition comprising organic material and from about 0.1 to about 5 percent by weight boron compound, said percentage based on the total weight of the composition, wherein the boron compound comprises boric oxide, boric acid, cationic salts of boric acid, or mixtures thereof, and wherein the cations have an atomic or molecular weight less than 130 atomic mass units (AMU).

19. A light stabilized composition exposed to acidic environmental conditions in a pH range of about 2 to about 5 comprising organic material and from about 0.1 to about 5 percent by weight boron compound, said percentage based on the total weight of the composition, wherein the boron compound comprises boric oxide, boric acid, cationic salts of boric acid, or mixtures thereof, and wherein the cations have an atomic or molecular weight less than 130 atomic mass units (AMU).

20. The composition according to claim 19 wherein the organic material is selected from the group consisting of plastics, rubbers, adhesives, coatings, waxes and dyes.

21. The composition according to claim 19 which also comprises from about 0.05 to 5 percent by weight of a hindered amine light stabilizer, said percentage based on the total weight of the composition.

22. The composition according to claim 21 wherein the hindered amine light stabilizer is bis (2,2,6,6-tetramethyl-4-piperidyl) sebacate or a mixture of poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidyl)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidyl)imino]]], butanedioic acid, dimethylester, and polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol.

23. The composition according to claim 21 which also comprises an ultraviolet light absorber.

24. The composition according to claim 23 wherein the ultraviolet light absorber is 2-(2H-Benzotriazole-2-yl)-4 methylphenyl.

25. The composition according to claim 21 wherein the boron compound content is in the range of about 1 to about 3 percent by weight, and the hindered amine light stabilizer content is in the range of about 0.1 to about 2 percent by weight, said percentages based on the total weight of the composition.

26. The composition according to claim 19 wherein the organic material is a polyolefin selected from the group consisting of polyethylene and polypropylene.

27. The composition according to claim 26 which also comprises from about 30 to about 80 percent by weight wood particles, said percentage based on the total weight of the composition.

28. The composition according to claim 27 which also comprises from about 0.05 to 5 percent by weight of a hindered amine light stabilizer, said percentage based on the total weight of the composition.

29. The composition according to claim 28 which also comprises an ultraviolet light absorber.

30. A wood-plastic composite article comprising from about 20 to about 70 percent by weight of a polyolefin selected from the group consisting of polyethylene and polypropylene, from about 30 to about 80 percent by weight wood particles, from about 0.1 to 5 percent by weight boron compound, from about 0.05 to 5 percent by weight of a hindered amine light stabilizer, and an ultraviolet light absorber, said percentages based on the total weight of the composition.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US05/23832

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : C08K 3/38, 5/3495 US CL : 524/99, 404, 405 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 524/99, 404, 405 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched None Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Please See Continuation Sheet		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,130,352 A (CHOW) 14 July 1992, claims 1-5 and column 4, lines 46-48	1-8
—		—
Y		9-30
X	US 6,262,161 B (BETSO et al.) 17 July 2001, claims 1,7, column 9, lines 65-67, column 10, lines 4-5, column 12, lines 49-63, column 13, lines 62-67, column 14 lines 47-61, column 16, lines 11-36.	1-6, 9-12, 14-15, 17-21, 23, 25-26, 30
—		—
Y		13, 22
X	US 6,780,913 B (SAWADA et al.) 24 August 2004, claims 1,4,5, column 7, lines 39-67, column 12, lines 6-10, 40-45, 61-67, column 13, lines 1-16	1-6, 9-15, 17-23, 25-26, 30,
—		—
Y		24
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"E" earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	
"O" document referring to an oral disclosure, use, exhibition or other means	"Z" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
09 January 2006 (09.01.2006)	19 JAN 2006	
Name and mailing address of the ISA/US	Authorized officer	
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450	Peter Szekely	
Facsimile No. (571) 273-3201	Telephone No. (703) 308-0661	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US05/23832

Continuation of B: **FIELDS SEARCHED** Item 3:

WEST

Search Terms: boric or borate or borax and hindered amine and wood or cellulose